Next Generation SCR-Dosing System Investigation

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Project ID: ACS 027

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Project Overview

Timeline

- Start – Oct 2014
- End – Sept 2017

Budget

- Matched 80/20 by USCAR as per CRADA agreement
- DOE funding for FY17: $200K;

Barriers

Addressed in next slide

Partners

- Pacific Northwest National Laboratory
- USCAR

Barriers - Relevance

- Selective Catalytic Removal of NO_x:

  $$4\ NO + \mathbf{4\ NH_3} + O_2 \rightarrow 6\ N_2 + 6H_2O$$

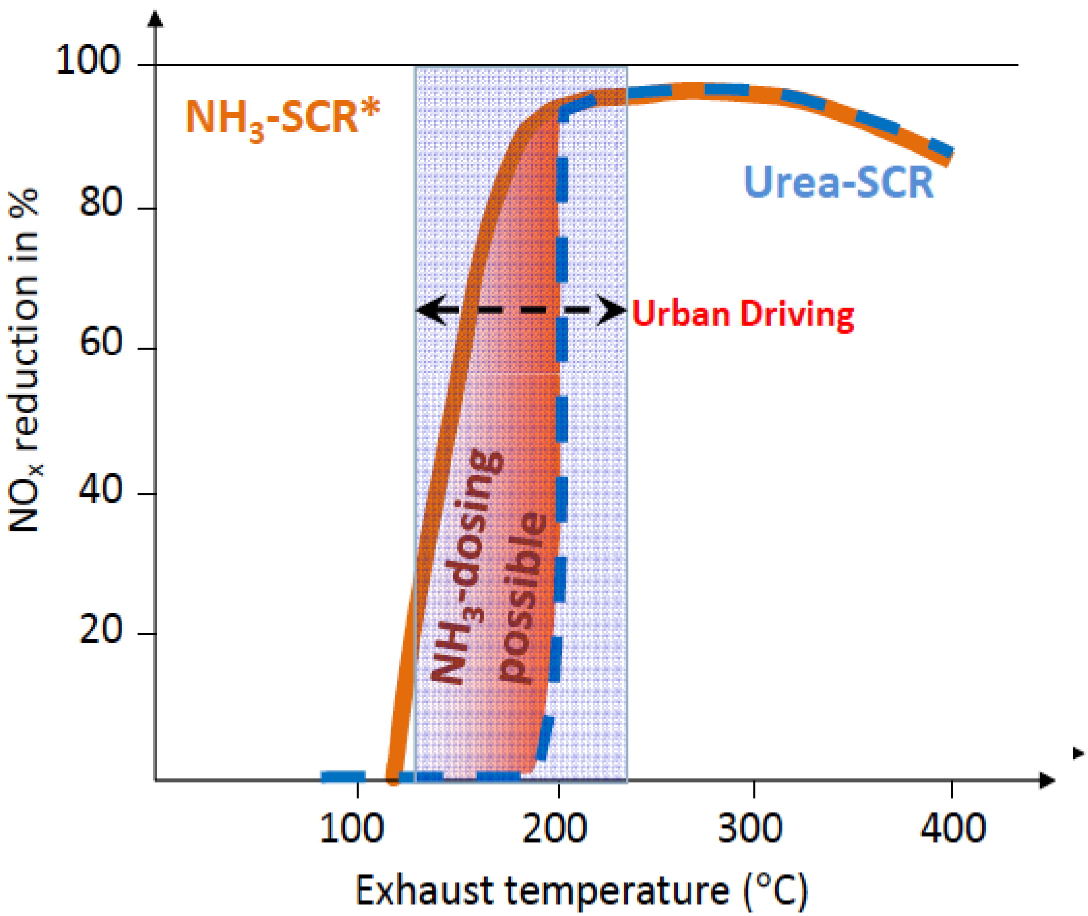
- NOx reduction systems (SCR) will require **improved ammonia storage and low temperature delivery**.
- Needed for diesel and lean-burn engines
- Challenge: Safe and efficient ammonia storage and delivery

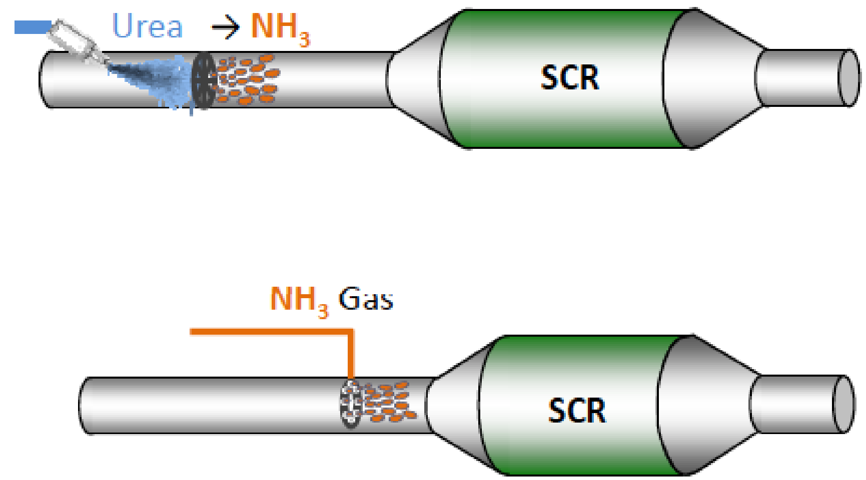
\- Urea solution (DEFBlue or Adblue®) [Urea+ ~70% water] mitigates most issues

- New materials as needed to solve issues with aqueous urea
- Compact NH_3 storage coupled with long driving range will help minimize fuel consumption

Direct NH_3 dosing

NO$_x$ Reduction vs. Exhaust Temperature





Direct NH$_3$-dosing enables good SCR performance during urban driving without deposit risk.

* NH$_3$-SCR efficiency: W. Tang et al. BASF, DOE-DEER conference, October 4th 2011, p.3

Goals and Objectives

- Develop alternative ammonia carrier materials for low temperature NH_3 dosing system
- 32.5 wt% aqueous Urea contains 17wt% NH_3 (gravimetric) and 200 kg/m^3 (volumetric): Any proposed materials should exceed these targets.
- Help develop the next generation SCR dosing system for improved low-temperature performance
- Convenient handling and distribution of ammonia carriers, and reduced overall system volume, weight, and cost
- Structural integrity of material

FEV solid SCR system: Ammonium carbamate

Liquid urea (DEF)

Need for new materials

- Existing materials have limitations
- New materials and composites are needed to address these limitations
- Synthesis of Eutectics and double salts
- Ammonia Absorption into Alkaline Earth Metal Halide Mixtures as an Ammonia Storage Material *Chun Yi Liu and Ken-ichi Aika Ind. Eng. Chem. Res. 2004, 43, 7484-7491*
- Development of new additives to enhance kinetics, thermodynamics and stability
- Ammonia Adsorption on Ion Exchanged Y-zeolites as Ammonia Storage Material *Chun Yi Liu and Ken-ichi Aika Journal of the Japan Petroleum Institute, 46, (5), 301-307 (2003*
- Theory can help identify potential systems
- *Designing mixed metal halide ammines for ammonia storage using density functional theory and genetic algorithms Peter Bjerre Jensen,Steen Lysgaard,Ulrich J. Quaade and Tejs Vegge, Phys.Chem.Chem.Phys.,2014,16, 19732—19740*

Approach

- Evaluate existing materials based on USCAR recommendations
- Synthesize new materials and composites to improve on existing materials

Develop testing protocol to:

- Determine ammonia storage capacity: wt.%/vol.%
- Determine ammonia release: temp, rate, energy requirement
- Solid material volume change during charge/discharge
- Stability and Safety: volatility under storage & handling conditions extended temp.
- Utilize expertise and state-of-the-art characterization and testing facilities at PNNL to address structure/function and performance
  - XRD, NMR, NH_3 TPD, DSC-TGA with MS
  - Time resolved FTIR studies for kinetics
  - Calorimetric studies for thermodynamics
  - Volumetric gas analyzer for vapor pressure studies

DEFBlue™ Vs. $MgCl_2.6NH_3$

30% Aqueous Urea

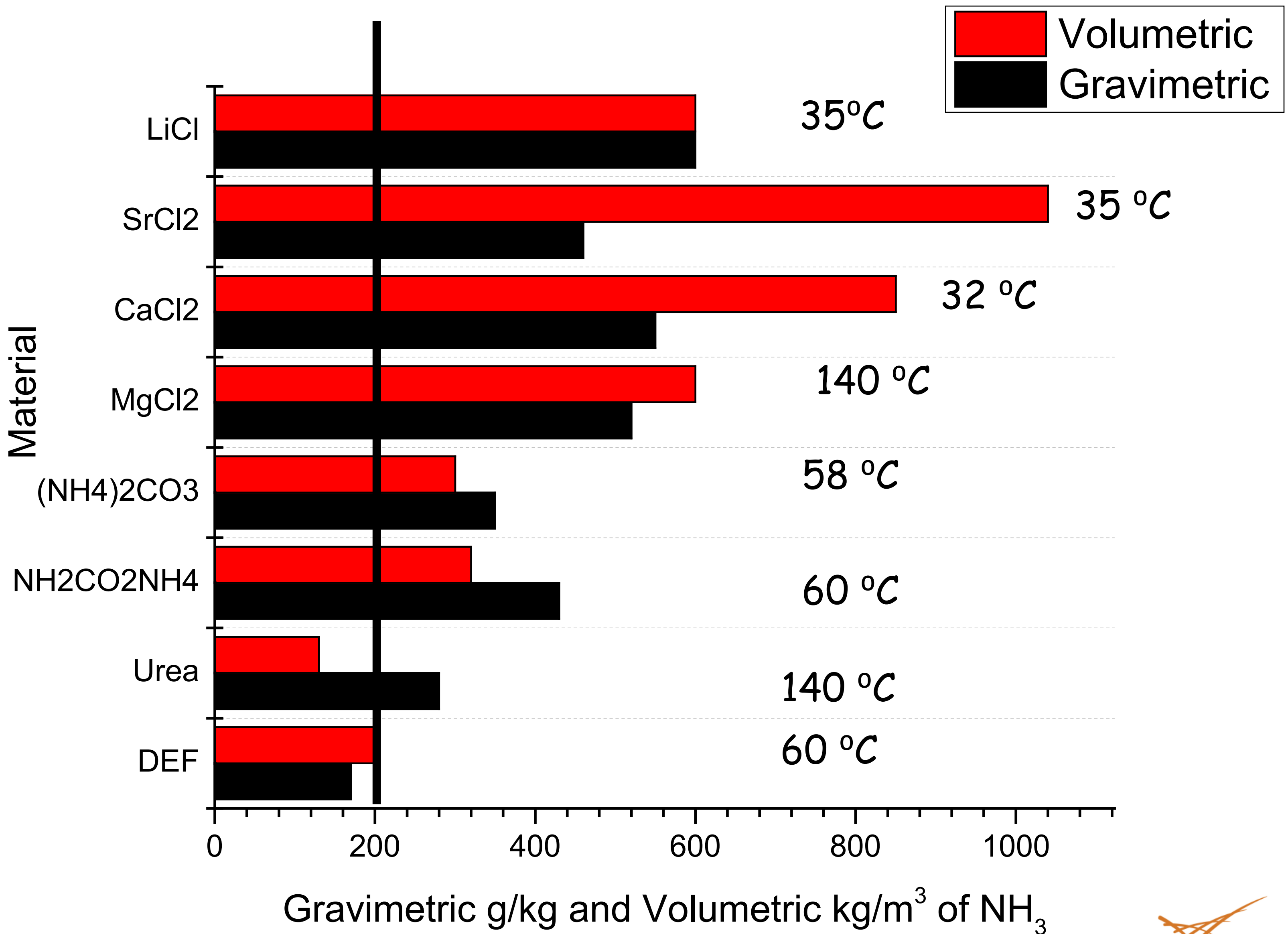
- 200 kg NH_3/m^3
- 17 wt% NH_3 (on composition basis)
- Convenient
- Freezing
- Solid deposits
- Lowering of exhaust temp due to water

$MgCl_2.6NH_3$

- ~ 600 kg NH_3/m^3
- 50 wt% NH_3 (on composition basis)
- Multi-step decomposition
- No complex chemistry
- Easily available $MgCl_2$ (10% of sea salt) and NH_3
- Freezing a non-issue

We use DEF to benchmark our materials

Summary of material properties

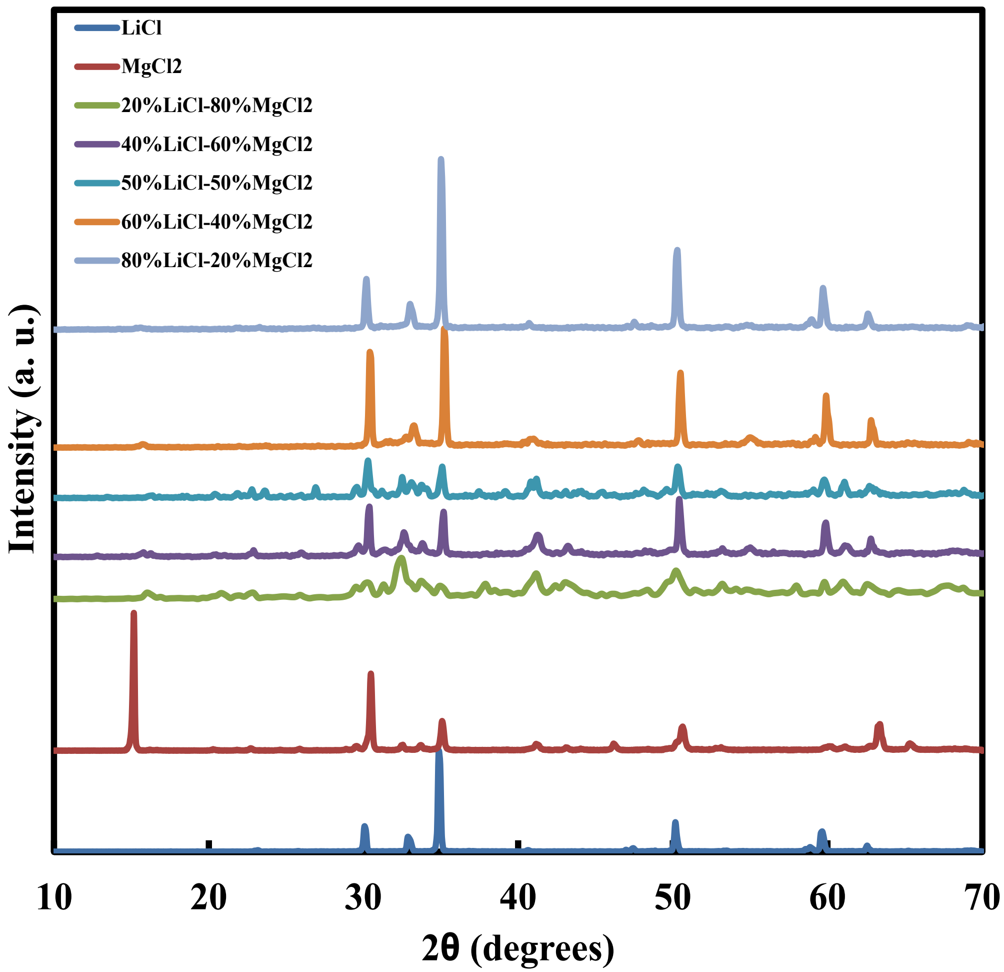


FY 2017 Accomplishments

- Tunable release of NH_3 release temperature.
- Transition metal containing double salts bind NH_3
- Characterize and Study the NH_3 uptake capacity of the Eutectic salts.
- Evaluated ammonia storage capacity of oxide based materials
- Completed recycle studies on compacted pellets
- Identify and quantify and mitigate HCl being released
- Evaluated
  - Effect of CO_2 on material performance
  - Effect of NOx, H_2O, CO on material performance

Synthesis of LiCl-$MgCl_2$ Double Salts

Vehicle Technologies Office



Powder XRD Pattern – LiCl-$MgCl_2$ Double Salts

- Synthesized double salts of xLiCl: y$MgCl_2$
- Novel phases identified
- 60% and 80% LiCl compositions predominantly LiCl
- Evaluating patterns and structures by Rietveld refinement
- Rapid NH_3 uptake
- Role of solvent: H_2O vs NH_3

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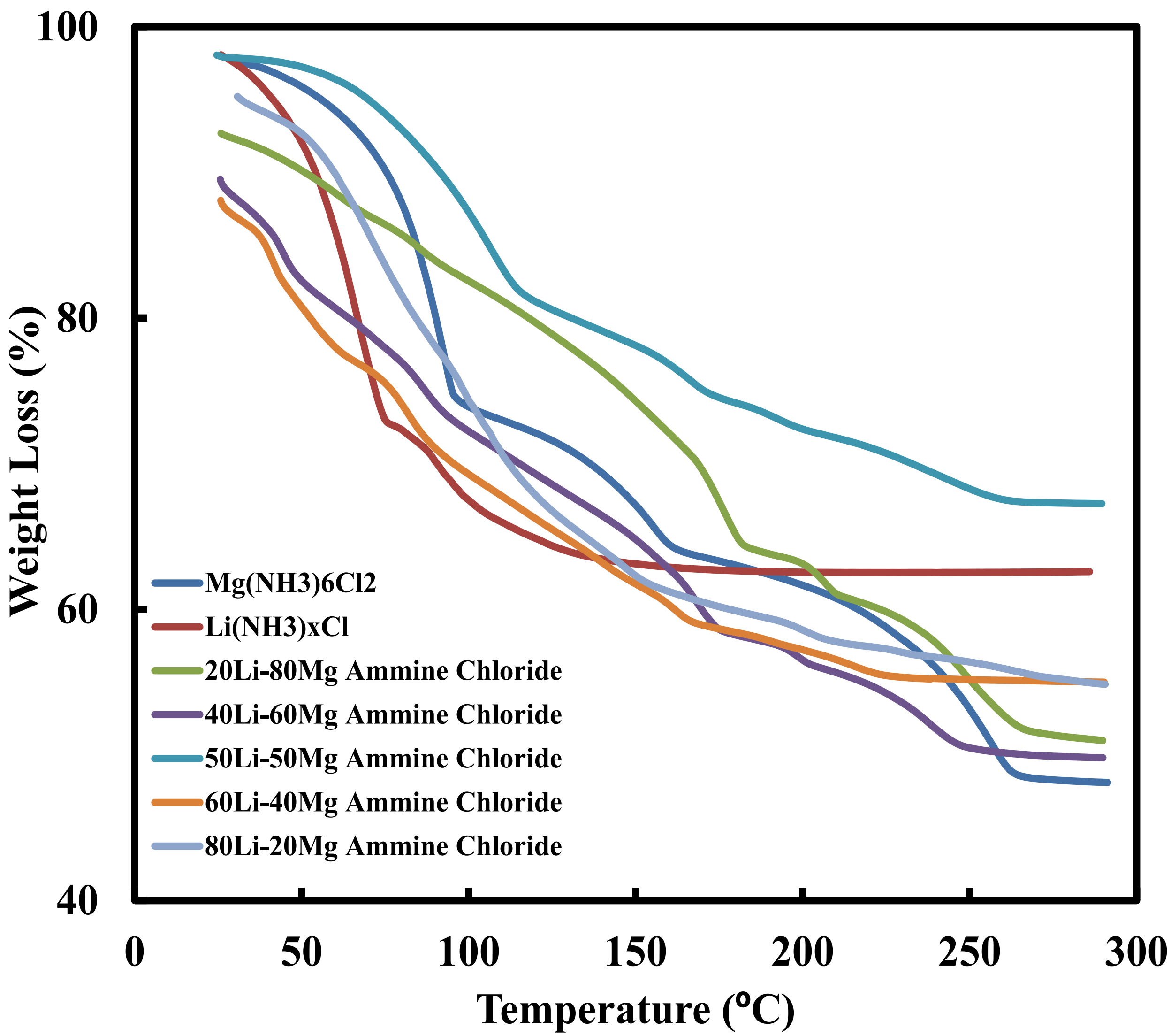
Ammonia Storage of LiCl-$MgCl_2$ Double Salts

Vehicle Technologies Office



Ammonia release profiles for LiCl-$MgCl_2$ Double Salts

- 30-50 wt% NH_3 sorption capacity achieved
- 1:1 LiCl:$MgCl_2$ shows lowest capacity (30 wt%)
- Temperature profiles can be tuned based upon composition
- Volume expansion is minimized in double salts
- Residual water (solvent) removal challenging exploring liquid anhydrous ammonia

Temperature of release tunable by composition

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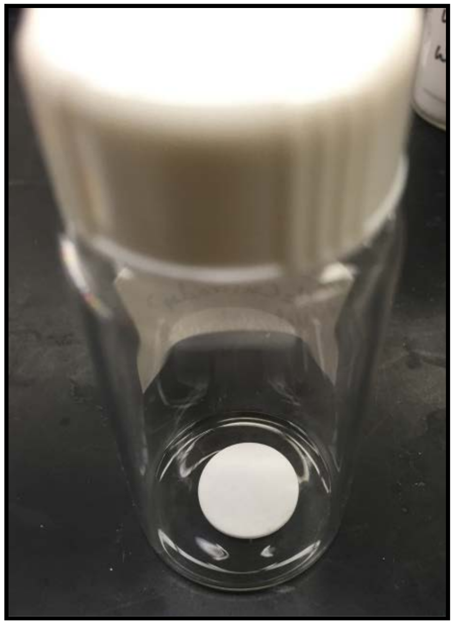
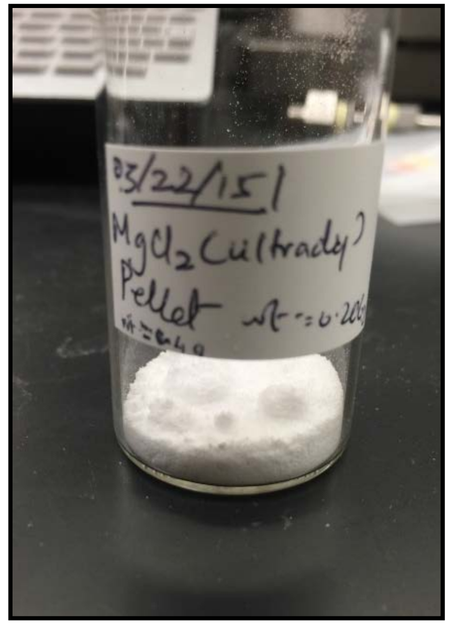
Effect of NH_3 on pellets



- Pellet-$MgCl_2$
- Before NH_3 adsorption
- Wt.=0.205 g
- Dia.= 9 mm
- Height = 0.05 mm

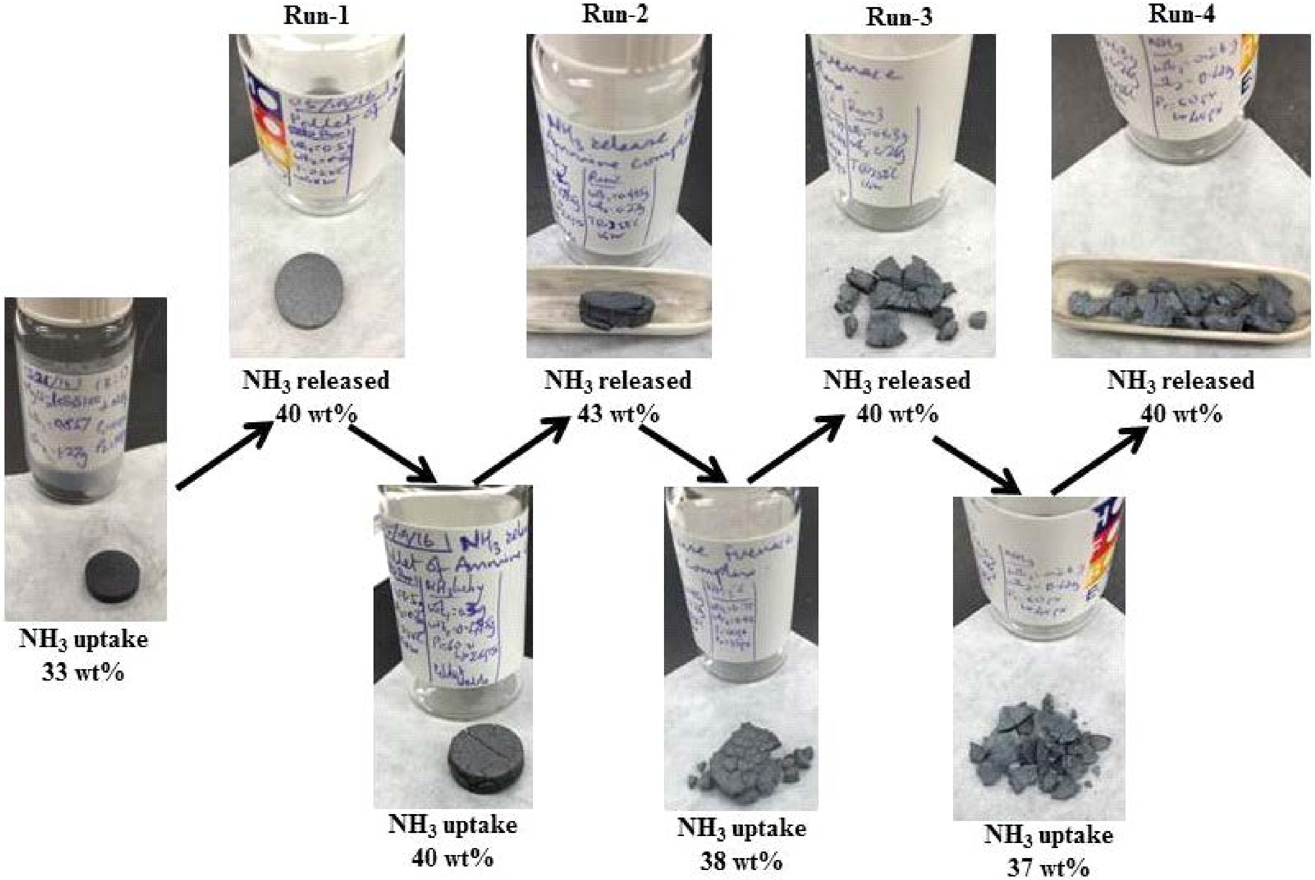


- Pellet-$MgCl_2$
- After NH_3 adsorption
- Wt.=0.4 g

- Loses engineered form ✗
- Only NH_3 released ✓
- > 50 wt% gravimetric capacity ✓
- Reversible ✓

New additives are needed to retain engineered form

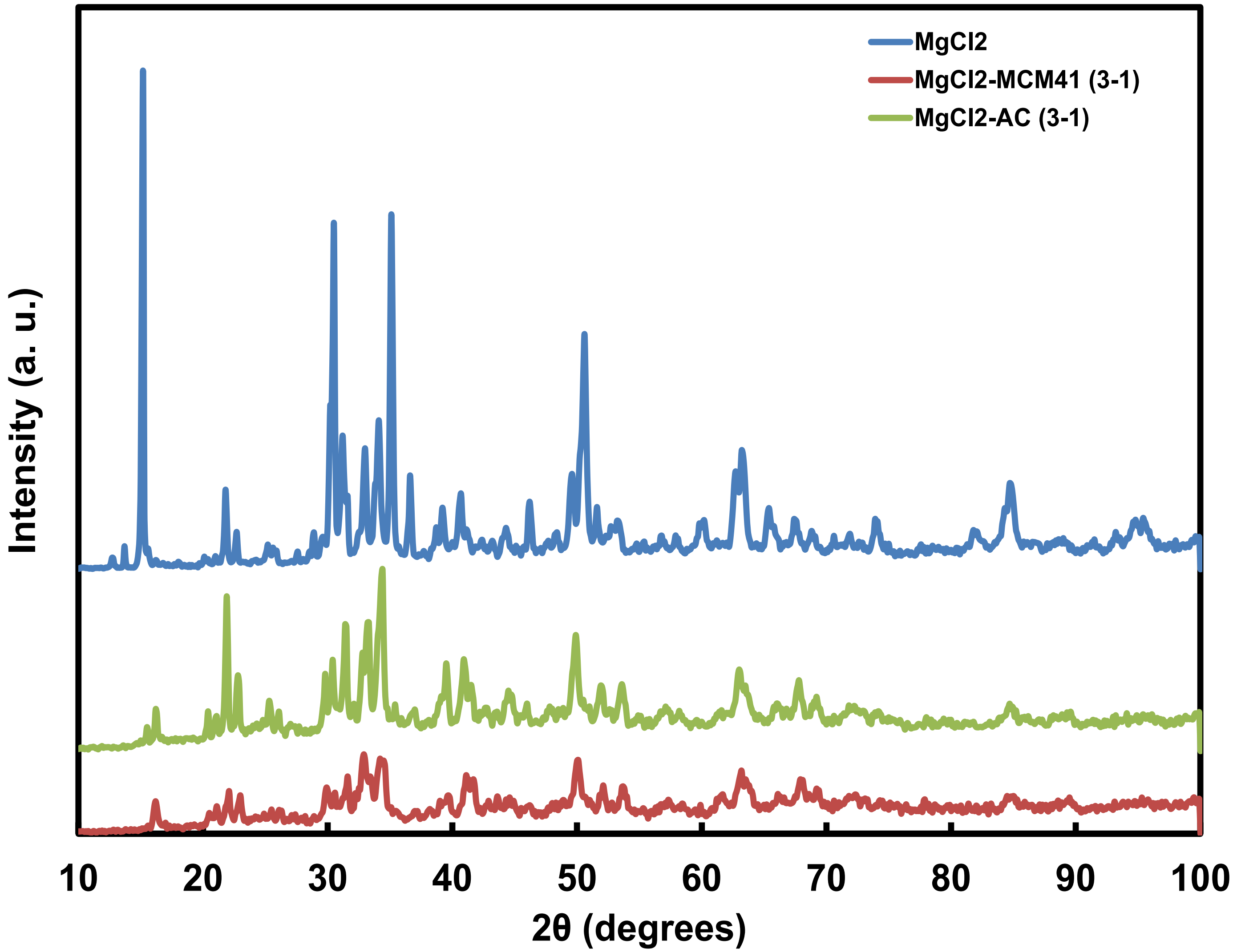
Recycle Studies



- The recycle studies were carried out on $Mg(NH_3)_6Cl_2$:KBB100 (3:1) sample.
- Mg-ammine composite was pressed into a pellet which was subjected to number of NH_3 release (at 250ºC) and uptake cycles.
- The pellet retains its engineered form for couple of cycles, but eventually crumbles into pieces.
- However, the recycle studies show that NH_3 uptake and storage capacity is not affected after 4 cycles.

Shape retention feasible; further optimization ongoing

Comparison of XRD Patterns



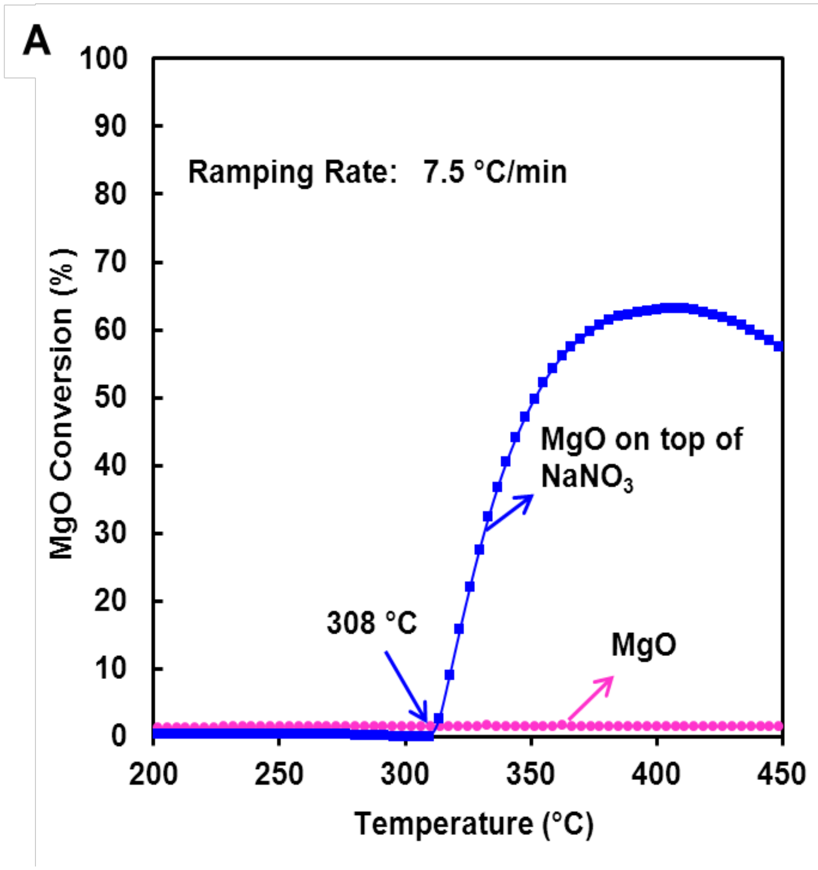
Retention of $MgCl_2$ phase through nano-composite formation

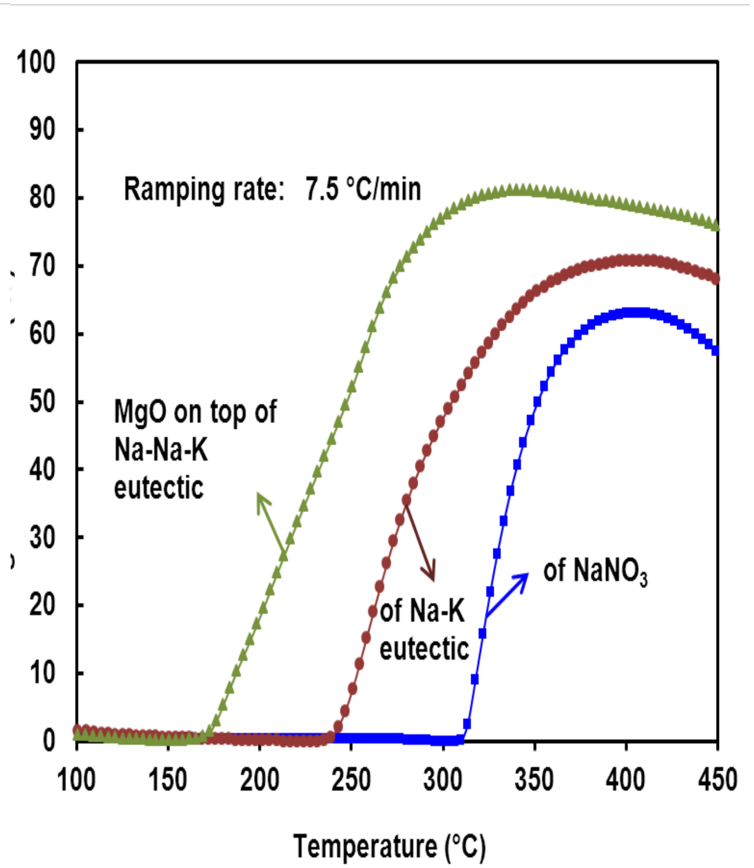
Impact of Exhaust Gases

- Ammonia storage materials ideally will not be exposed to exhaust gases
- In event of exposure to exhaust gases we evaluated impact on material performance
- Effect of CO_2 on material performance
  - no impact on capacity/performance
- Effect of NOx, H_2O, CO on material performance
  - NO_2 shows formation of nitrate and nitrite species
  - NO has no impact on performance and capacity
  - CO has no impact on performance and capacity
  - H_2O results in decreased capacity due to competition
    - HCl formation and release increases

Water remains to be a challenge

CO_2 absorption on MgO Eutectics



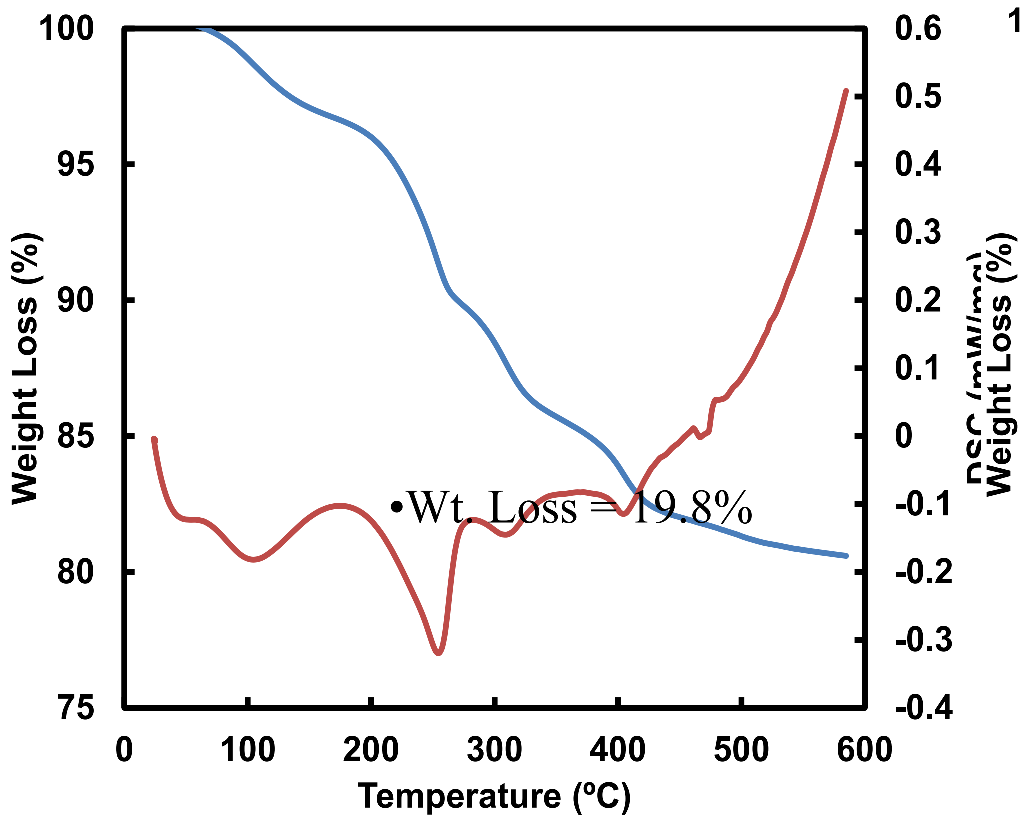


- CO_2 absorption on MgO with $NaNO_3$
- Decrease in temperature of CO_2 uptake

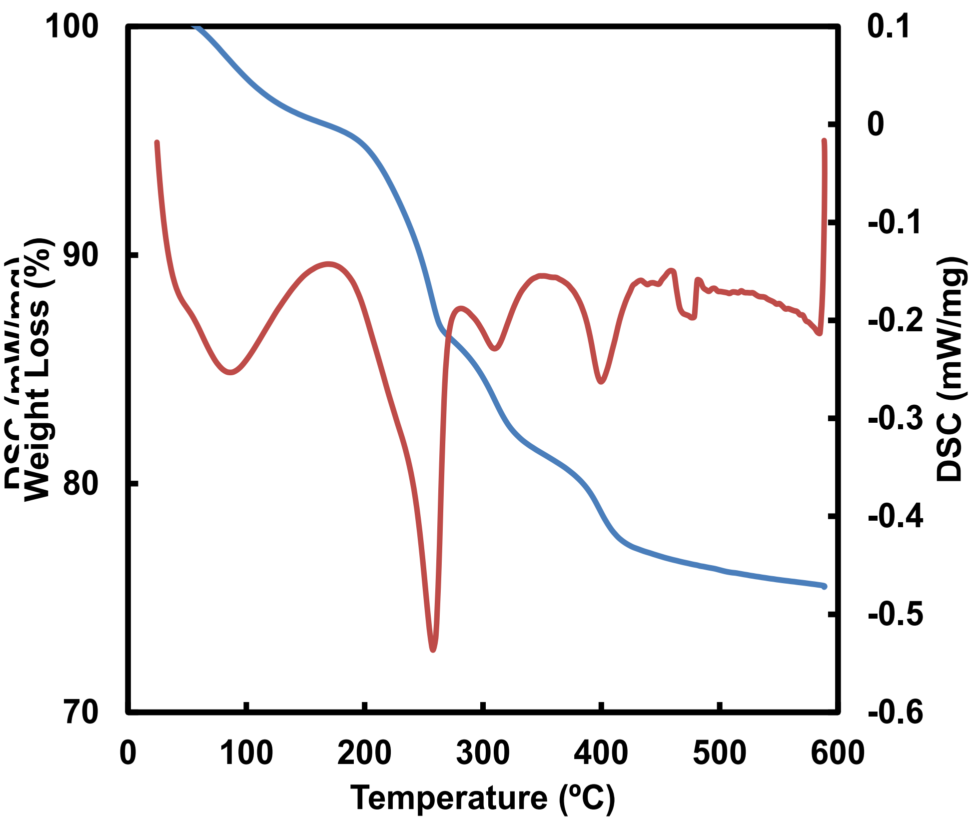
- CO_2 absorption on MgO with various salts
- Ability to tune temperature of CO_2 uptake

MgO + Molten Salts

MgO + NH_4 Acetate



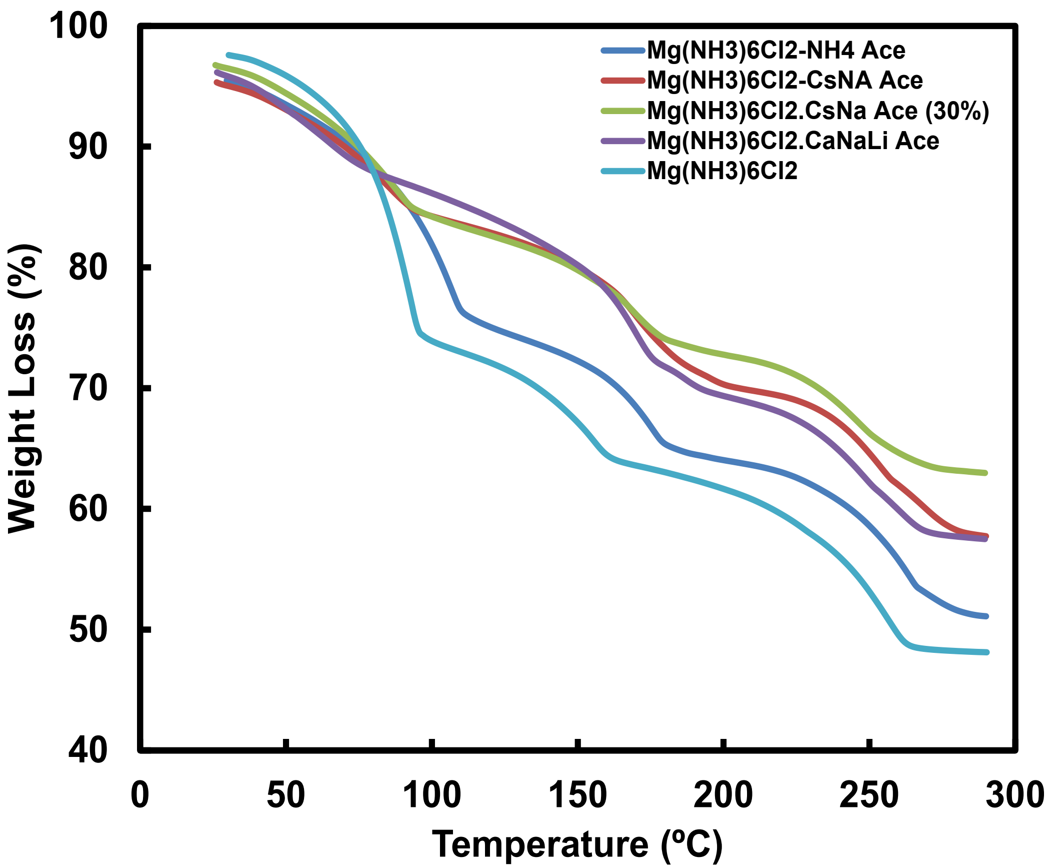
MgO + NH_4 Acetate + NH_3

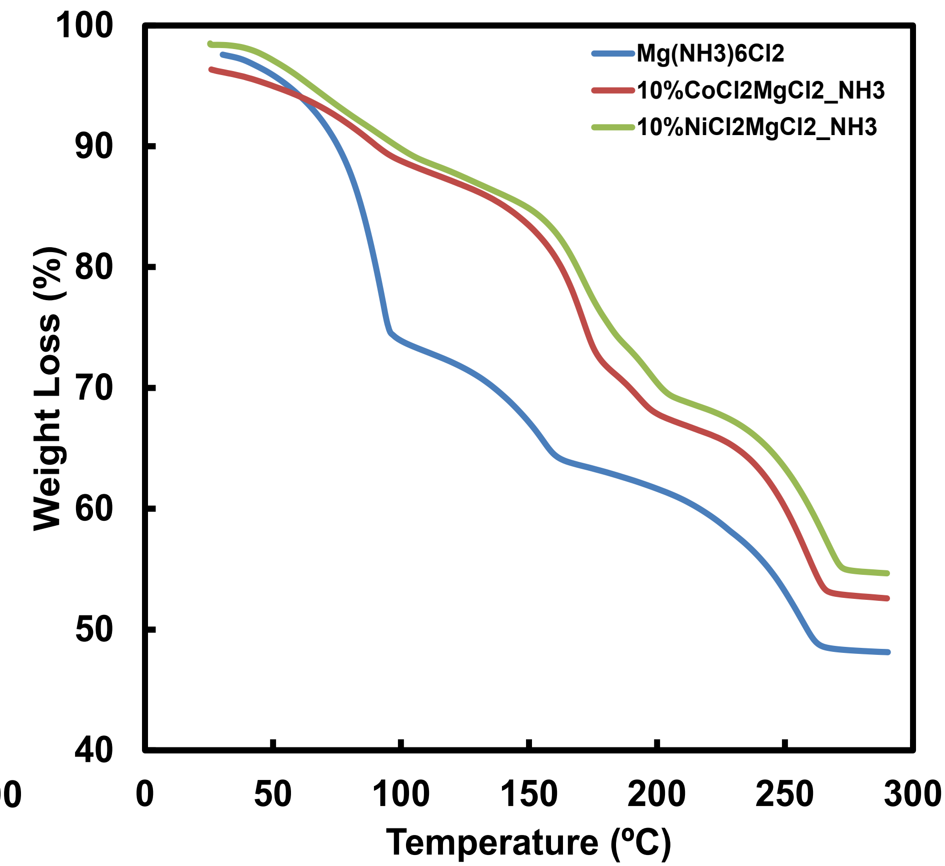


Attempts to utilize oxide materials not successful

NH_3 Storage: $MgCl_2$+Molten salts and $MgCl_2$ Double salts

Vehicle Technologies Office





- Multiple additives were screened to tune NH_3 release properties
- Temperature of NH_3 release tuned from 100 ºC to 150 ºC

Ability to design NH_3 release based on catalyst needs

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Reviewer Comments

- The approach to most of the work is very good and has even focused on making new materials.
- "Cast a wider net"
- Project needs to consider non-chlorine materials that will not produce hydrogen chloride (HCl)
- Downgrading carbamate as a urea replacement, because it yields CO_2 as a decomposition product, is not appropriate

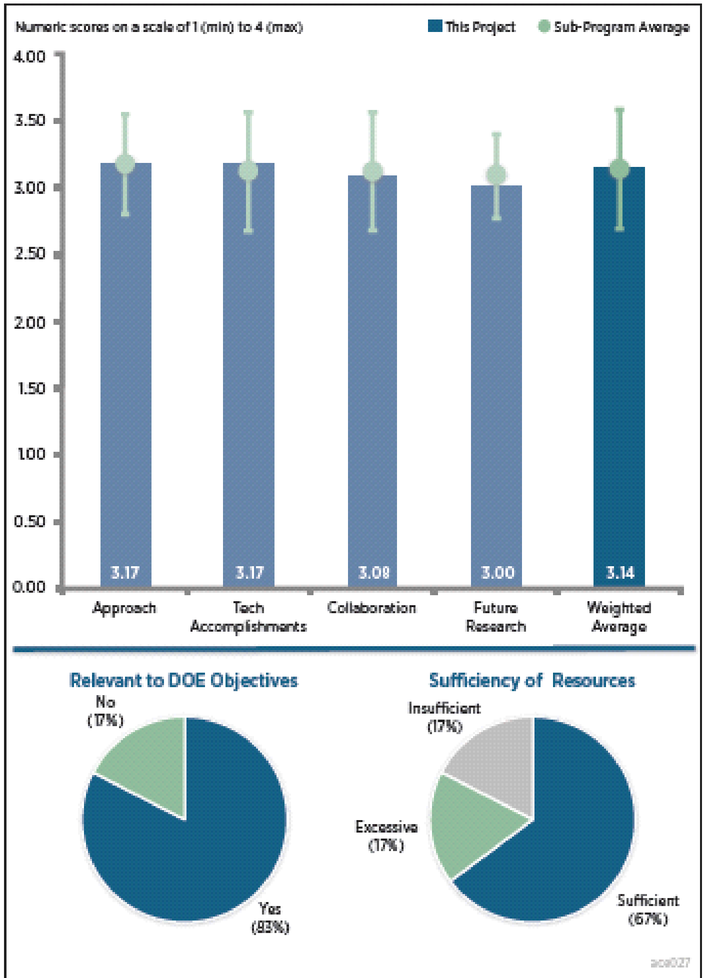

Figure 4-19 - Next Generation SCR-Dosing System Investigation: Abhijeet Karkamkar (Pacific Northwest National Laboratory) - Advanced Combustion Engines

Response to Reviewer Comments

- HCl: We quantified HCl, developed pathways to mitigate HCl
- Synthesized, characterized and evaluated oxide based materials and composites
- Down-selection criterion: Deposition of ammonium carbamate was identified by USCAR as a serious issue

Collaborations/Interactions

OEM

Development Teams and Suppliers

Project Management PNNL

USCAR

•Provide results of current performance metrics of various NH_3 storage materials and feedback on material performance

PNNL

Carry out and disseminate results of synthesis, characterization, testing and provide recommendations to USCAR

- Monthly updates and teleconference with USCAR PI
- Quarterly teleconference with USCAR SCR team
- Bi-annual F2F meeting with USCAR SCR team

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Future Work

1. **Composites, Double Salts and Eutectics: Theory would provide critical synthetic insight**
2. **System design: Identified suitable composites for system design**
3. **Material cost analysis:**

Any proposed future work is subject to change based on funding levels

Summary

Vehicle Technologies Office

- Completed the synthesis and evaluation of several Eutectic and double salts.
- Characterized the NH_3 uptake capacity of the Eutectic salts.
- Evaluated ammonia storage capacity of oxide based materials
- Evaluated ammonia storage capacity of oxide based materials
- Completed recycle studies on compacted pellets
- Evaluated
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